Indian J. Phys. **51B**, 293-301 (1977)

Force constants, compliance constants, coriolis constants, vibrational amplitudes and shrinkage effect for transition metal ammine complexes

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The general valence force field constants compliance constants, coriolis constants vibrational amplitudes and shrinkage effect for Transition metal ammine complexes have been evaluated following L-F approximation method. The results thus obtained are compared with those obtained from the available pseudo–exact force constants. It has been found that these are well comparable. The trend of vibration in the force constants among the complexes under present study has been studied. The dependence of force constants on the number of d-electrons has also been discussed.

A thorough investigation of skeletal infrared and Raman data, force constants and bond properties has been made recently by Schmidt & Müller (1975) for octahedral hexaammine and tetrahedral and square-planar tetraammine complexes of the Transition metals (including Zinc and Cadmium) for which reliable vibrational frequencies are known. In the present communication it is aimed to evaluate force constants, compliance constants, coriolis constants, vibrational amplitudes and shrinkage effect for these complexes. The GVFF force constants and compliance constants, evaluated by L-F approximation method, (Pandey *et al.*) have been compared with those obtained from recently available pseudo exact force constants [Müller *et al.* (1975); Schmidt & Müller (1974)] in order to examine the validity of the method followed.

Wilson's GF matrix method (1955) has been employed to calculated the force constants in the GVFF. L-F approximation method given by Pandey *et al.* have been adopted in the solution of 2×2 secular determinant. The compliance matrix C has been obtained by inverting the F matrix and the

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compliance constants from the secular equation $|G^{-1}C - \Phi E| = 0$. The vibrational mean amplitudes at different temperatures have been computed by L-matrix method [Peacock & Müller (1968)] and Cyvin's procedure (1968). The coriolis constants and shrinkage effect have been evaluated following Cyvin's method (1968). The vibrational frequencies employed in the present study are taken from Schmidt & Müller (1975) and are collected in table 1.

Table 1. Vibrational Frequencies (in cm^{-1}) of Octahedral Hexaammine, Tetrahedral Tetrammine and Square—Planar Tetraammine Complexes

Complex	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$
$[Mn(NH_3)_6]^{2+}$	330	235	302	165		
$[Fe(NH_3)_6]^{2+}$	344	245	315	170		
$[Co(NH_3)_6]^{2+}$	357	255	325	192		
$[Ni(NH_3)_6]^{2+}$	370	265	334	215	235	166
$[Zn(NH_3)_6]^{2+}$	340	235	300	165		
$[Cd(NH_3)_6]^{2+}$	342	235	298	165		
$[Cr(NH_3)_6]^{3+}$	465	412	468.5	268	270	206
$[Co(NH_3)_6]^{3+}$	494	442	474.7	331	322	277.6
$[Ru(NH_3)_6]^{3+}$	500	475	463	273	248	175
$[Rh(NH_3)_6]^{3+}$	514	483	472	294.5	240	169.7
$[Os(NH_3)_6]^{3+}$	515	490	452	256		
$[Ir(NH_3)_6]^{3+}$	527	500	475	272	262	185
$[Pt(NH_3)_6]^{4+}$	569	545	530	318	288	203.5
	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$		
$[Co(NH_3)_4]^{2+}$	405	195	430	195		
$[Zn(NH_3)_4]^{2+}$	431.2	156.5	411.5	156.5		
$[Cd(NH_3)_4]^{2+}$	386	170	269.5	163		
	$\nu_1(A_{1g})$	$\nu_2(B_{1g})$	$\nu_3(B_{2g})$	$\nu_4(A_{2u})$	$\nu_6(E_u)$	$\nu_7(E_u)$
$[Cu(NH_3)_4]^{2+}$	420	375		226	425.5	256
$[Pd(NH_3)_4]^{2+}$	510	468	305	237	494	291
$[Pt(NH_3)_4]^{2+}$	538	526	270	235	510	297

The results of the general valence force field constants, compliance constants of octahedral hexaammine, tetrahedral tetraammine and square-planar tetraammine complexes are collected in tables 2 and 3 and compared with those obtained from pseudo-exact force constants. It is noted from the

tables 2 and 3, that they are in good agreement. The force constants are a convenient measure of the strength of a chemical bond and, therefore, it is interesting to study the trend of the force constants among the complexes under study. Some interesting aspects can be summarized as follows :

Table 2. General Valence Force Field Constants (in mdyn/A) of Octahedral Hexaammine, Tetrahedral Tetraammine and Square-Planar Tetraammine Complexes and comparison with those obtained from Pseudo—exact force Constants*

Octahedral Hexaammine Complex	f r	f rr	f' rr	f −f'' r∝ r∝	f f' ∝ ∝∝	f −f' ∝∝ ∝∝	f' f' ∝∝ ∝∝
$[Mn(NH_3)_6]^{2+}$	0.666	0.090	0.068	0.026			
$[Fe(NH_3)_6]^{2+}$	0.725	0.097	0.072	0.027			
$[Co(NH_3)_6]^{2+}$	0.787	0.104	0.074	0.034			
$[Ni(NH_3)_6]^{2+}$	0.843	0.111	0.084	0.042	0.136	−0.001	−0.001
	(0.863)	(0.123)	(0.013)				
$[Zn(NH_3)_6]^{2+}$	0.689	0.101	0.067	0.024			
$[Cd(NH_3)_6]^{2+}$	0.730	0.103	0.031	0.019			
$[Cr(NH_3)_6]^{3+}$	1.640	0.078	0.219	0.068	0.207	−0.003	0.012
	(1.723)	(0.078)	(0.133)				
$[Co(NH_3)_6]^{3+}$	1.832	0.081	0.290	0.097	0.289	0.014	0.014
	(1.951)	(0.081)	(0.171)				
$[Ru(NH_3)_6]^{3+}$	2.000	0.041	0.345	0.054	0.201	0.023	0.023
$[Rh(NH_3)_6]^{3+}$	2.087	0.052	0.357	0.062	0.218	0.037	0.037
$[Os(NH_3)_6]^{3+}$	2.124	0.042	0.368	0.034			
$[Ir(NH_3)_6]^{3+}$	2.272	0.046	0.329	0.038	0.228	0.028	0.028
$[Pt(NH_3)_6]^{4+}$	2.747	0.044	0.322	0.050	0.300	0.046	0.046

Tetrahedral Tetraammine Complex	f r	f rr	f −f' ∝ ∝∝	f −f' r∝ r∝	f −f' ∝∝ ∝
$[Co(NH_3)_4]^{2+}$	1.439	0.069	0.123	−0.044	−0.002
$[Zn(NH_3)_4]^{2+}$	1.426	0.146	0.081	−0.027	0.0
	(1.502)	(0.122)			
$[Cd(NH_3)_4]^{2+}$	1.235	0.086	0.099	−0.022	0.002

*The values in parentheses indicate force constants obtained from pseudo-exact force field

Table 2—(*Contd.*)

Square-Planar Tetraammine Complex	f_r	f_{rr}	f'_{rr}	$f_{r\alpha} - f'_{r\alpha}$	$-(f_{\alpha\alpha} - f'_{\alpha\alpha})$	$f_{\alpha\alpha} - f'_{\alpha\alpha}$	f_{γ}
$[Cu(NH_3)_4]^{2+}$	1.408 (1.365)	0.183 (0.225)	0.090	0.866		0.244	0.061
$[Pd(NH_3)_4]^{2+}$	2.144 (2.166)	0.260 (0.237)	0.130	1.332	0.558	0.342	0.086
$[Pt(NH_3)_4]^{2+}$	2.537	0.303	0.032	1.580	0.855	0.385	0.103

Table 3. Compliance Constants (Å/mdyn) of Octahedral Hexaammine, Tetrahedral Tetraammine and Square-Planar tetraammine complexes and Comparison with those obtained from Pseudo—exact force constants*

Octahedral Hexaammine Complex	C_r	$-C_{rr}$	$-C'_{rr}$	$C_{r\alpha} - C''_{r\alpha}$	$C_{\alpha} - C''_{\alpha\alpha}$	$C_{\alpha\alpha} - C''_{\alpha\alpha}$	$C'_{\alpha\alpha} - C''_{\alpha\alpha}$
$[Mn(NH_3)_6]^{2+}$	1.641	0.148	0.133	0.591			
$[Fe(NH_3)_6]^{2+}$	1.504	0.136	0.116	0.933			
$[Co(NH_3)_6]^{2+}$	1.388	0.125	0.105	0.470			
$[Ni(NH_3)_6]^{2+}$	1.301 (1.400)	0.115 (0.142)	0.112 (0.099)	0.423	7.612	0.189	0.189
$[Zn(NH_3)_6]^{2+}$	1.589	0.157	0.098	0.504			
$[Cd(NH_3)_6]^{2+}$	1.475	0.159	0.012	0.299			
$[Cr(NH_3)_6]^{3+}$	0.649 (0.667)	0.021 (0.021)	0.104 (0.121)	0.257	5.00	0.153	−0.232
$[Co(NH_3)_6]^{3+}$	0.589 (0702)	0.017 (0.035)	0.113 (0.123)	0.214	3.620	−0.114	−0.112
$[Ru(NH_3)_6]^{3+}$	0.525	0.007	0.097	0.136	5.323	−0.592	−0.579
$[Rh(NH_3)_6]^{3+}$	0.503	0.008	0.093	0.127	5.233	−0.844	−0.844
$[Os(NH_3)_6]^{3+}$	0.489	0.006	0.087	0.077			
$[Ir(NH_3)_6]^{3+}$	0.453	0.007	0.067	0.059	4.682	−0.570	−0.555
$[Pt(NH_3)_6]^{4+}$	0.372	0.005	0.045	0.054	3.694	−0.557	−0.556

Tetrahedral Tetraammine Complex	C_r	$-C_{rr}$	$C_{\alpha} - C'_{\alpha}$	$C_{r\alpha} - C'_{r\alpha}$	$C_{\alpha\alpha} - C'_{\alpha\alpha}$
$[Co(NH_3)_4]^{2+}$	0.712	0.035	8.347	0.267	0.242
$[Zn(NH_3)_4]^{2+}$	0.729 (0.843)	0.064 (0.103)	12.518	0.269	0.154
$[Cd(NH_3)_4]^{2+}$	0.825	0.052	10.107	0.191	−0.119

*The values in parertheses indicate compliance constants calculated from pseudo exact force constants.

Table 3—A(*Contd.*)

Square--Planar Tetraammine Complex	C r	-C rr	C' rr	C -C' r∝ r∝	C C ∝∝ ∝∝	C-C' ∝ ∝∝	C γ
$[Cu(NH_3)_4]^{2+}$	0.742 (0.759)	0.105 (0.123)	0.036 (0.036)	0.599		4.250	16.174
$[Pd(NH_3)_4]^{2+}$	0.479 (0.481)	0.195 (0.198)	0.018 (0.018)	0.381	1.143	2.971	11.642
$[Pt(NH_3)_4]^{2+}$	0.401	0.049	0.004	0.318	1.066	2.610	9.740

1. The metal nitrogen stretching force constants, f(MN) for ammine complexes with the same symmetry with central atoms having the same oxidation state and belonging to the same transition series are nearly equal.

2. The force constants for hexaammine complexes of trivalent first transition series metal ions are higher as compared with those for hexaammines of divalent ions. This is on account of the effect of oxidation number on the metal ligant stretching force constants.

3. The dependence of the force constants f(MN) for hexaammine complexes on number of d-electrons can be studied for $[Mn(NH_3)_6]^{2+}$ (d^5, 0.67); $[Fe(NH_3)_6]^{2+}$ (d^6, 0.72); $[Co(NH_3)_6]^{2+}$ (d^7, 0.79); $[Ni(NH_3)_6]^{2+}$ (d^8, 0.84); and $[Zn(NH_3)_6]^{2+}$ (d^{10}, 0.69) where the values in parantheses are the number of d-electrons and stretching force constant respectively. The trend of variation of the stretching force constant for these hexaammine complexes with number of d-electrons is shown in figure 1. The result is inconsistent with the crystal-field stabilization energy (1966) viz. 0Dq for d^5 and d^{10} configurations, 4Dq for d^6 configuration, 6Dq for d^7 configuration and 12Dq for d^8 configuration for octahedral stereochemistry. From the above trend it is inferred that the strength of the chemical bonds is in the order :

$$Ni - N > Co - N > Fe - N > Zn - N > Mn \quad N.$$

4. For the complexes of transition metals in the same group of periodic table, the metal-ligand stretching force constant increases from lighter to heavier central atom in the series :

   (i) $[Co(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$ and $[Ir(NH_3)_6]^{3+}$; (ii) $[Ru(NH_3)_6]^{3+}$ and $[Os(NH_3)_6]^{3+}$ and (iii) $[Pd(NH_3)_4]^{2+}$ and $[Pt(NH_3)_4]^{2+}$.

5. The stretching force constant f(MN) increases as the coordination number increases for the ammine complexes under present study.

The coriolis constants $\zeta_3(F_{1u} \times F_{1u})$ and $\zeta_4(F_{1u} \times F_{1u})$ for octahedral hexaammine complexes, $\zeta_3(F_2 \times F_2)$ and $\zeta_4(F_2 \times F_2)$ for tetrahedral tetraammine complexes, and $\zeta_6(E_u \times E_u)$ and $\zeta_7(E_u \times E_u)$ for square-planar tetraammine complexes are given in table 4.

Table 4. Coriolis Constants for Octahedral Hexaamine, Tetrahedral Tetraamine and Square-planar Tetraammine Complexes

Octahedral Hexaammine Complexes	$\zeta_3(F_{1u} \times F_{1u})$	$\zeta_4(F_{1u} \times F_{1u})$
$[Mn(NH_3)_6]^{2+}$	0.425	0.075
$[Fe(NH_3)_6]^{2+}$	0.418	0.082
$[Co(NH_3)_6]^{2+}$	0.421	0.078
$[Zn(NH_3)_6]^{2+}$	0.380	0.094
$[Ni(NH_3)_6]^{2+}$	0.447	0.053
$[Cd(NH_3)_6]^{2+}$	0.257	0.242
$[Cr(NH_3)_6]^{3+}$	0.449	0.051
$[Co(NH_3)_6]^{3+}$	0.482	0.018
$[Ru(NH_3)_6]^{3+}$	0.288	0.212
$[Rh(NH_3)_6]^{3+}$	0.294	0.206
$[Os(NH_3)_6]^{3+}$	0.169	0.331
$[Ir(NH_3)_6]^{3+}$	0.171	0.320
Tetrahedral Tetraammine Complexes	$\zeta_3(F_2 \times F_2)$	$\zeta_4(F_2 \times F_2)$
$[Co(NH_3)_4]^{2+}$	0.291	0.208
$[Zn(NH_3)_4]^{2+}$	0.264	0.236
$[Cd(NH_3)_4]^{2+}$	0.175	0.325
Square-planar Tetraammine Complexes	$\zeta_6(E_u \times E_u)$	$\zeta_7(E_u \times E_u)$
$[Cu(NH_3)_4]^{2+}$	0.613	−0.613
$[Pd(NH_3)_4]^{2+}$	0.276	−0.276
$[Pt(NH_3)_4]^{2+}$	0.188	−0.168

Table 5. Vibrational Amplitudes (in Å) for Octahedral Hexaamine Tetrahedral Tetraammine and Square-planar Tetraammine Complexes

Complex	Distance	Mean Amplitudes of Vibration		
		T = 0°K	T = 298.15°K	T = 500°K
$[Mn(NH_3)_6]^{2+}$	(X–Y)	0.0675	0.0881	0.1092
	(Y . . Y) Linear	0.0873	0.1182	0.1475
$[Fe(NH_3)_6]^{2+}$	(X–Y)	0.0660	0.0848	0.1048
	(Y . . Y) Linear	0.0855	0.1139	0.1418
$[Co(NH_3)_6]^{2+}$	(X–Y)	0.0645	0.0827	0.1008
	(Y . . . Y) Linear	0.0838	0.1127	0.1365
$[Ni(NH_3)_6]^{2+}$	(X–Y)	0.0635	0.0795	0.0977
	(Y . . Y) Linear	0.0822	0.1064	0.1317
	(Y . . Y) Non-Linear	0.0896	0.1263	0.1416
$[Zn(NH_3)_6]^{2+}$	(X–Y)	0.0686	0.0866	0.1074
	(X . . Y) Linear	0.0938	0.1175	0.1467
$[Cd(NH_3)_6]^{2+}$	(X–Y)	0.0636	0.0834	0.1035
	(Y . . Y) Linear	0.0868	0.1174	0.1465
$[Cr(NH_3)_6]^{2+}$	(X–Y)	0.0539	0.0599	0.0713
	(Y . . . Y) Linear	0.0680	0.0773	0.0919
	(Y . . Y) Non-Linear	0.0802	0.1043	0.1291
$[Co(NH_3)_6]^{2+}$	(X–Y)	0.0522	0.0580	0.0696
	(Y . . . Y) Linear	0.0657	0.0734	0.0865
	(Y . . . Y) Non-Linear	0.0750	0.0926	0.1056
$[Ru(NH_3)_6]^{3+}$	(X–Y)	0.0495	0.0549	0.0645
	(Y . . Y) Linear	0.0640	0.0706	0.0825
	(Y . . Y) Non-Linear	0.0805	0.1099	0.1273
$[Rh(NH_3)_6]^{3+}$	(X–Y)	0.0489	0.0541	0.0633
	(Y . . Y) Linear	0.0634	0.0696	0.0811
	(Y . . . Y) Non-Linear	0.0809	0.1086	0.1294
$[Os(NH_3)_6]^{3+}$	(X–Y)	0.0478	0.0530	0.0622
	(Y . . . Y) Linear	0.0630	0.0690	0.0804
$[Ir(NH_3)_6]^{3+}$	(X–Y)	0.0469	0.0516	0.0602
	(Y . . . Y) Linear	0.0624	0.0680	0.0789
	(Y . . . Y) Non-Linear	0.0788	0.1039	0.1243

Table 5—(*Contd.*)

Complex	Distance	Mean Amplitudes of Vibration		
		T = 0°K	T = 298.15°K	T = 500°K
$[Pt(NH_3)_6]^{4+}$	(X–Y)	0.0446	0.0481	0.0553
	(Y . . .Y) Linear	0.0598	0.0642	0.0736
	(Y . . .Y) Neo-Linear	0.0750	0.0956	0.0995
$[Co(NH_3)_4]^{2+}$	(X-Y)	0.0548	0.0624	0.0742
	(Y . . .Y)	0.0840	0.1256	0.1447
$[Zn(NH_3)_4]^{2+}$	(X–Y)	0.0548	0 0628	0.0749
	(Y . . .Y)	0.0896	0 1480	0.1702
$[Cd(NH_3)_4]^{2+}$	(X-Y)	0.0553	0.0653	0.0789
	(Y . . .Y)	0.0885	0 1405	0.1621
$[Cu(NH_3)_4]^{2+}$	(X-Y)	0.0551	0 0632	0.0755
	(Y . . Y) Linear	0 0707	0.0821	0.0986
$[Pd(NH_3)_4]^{2+}$	(X-Y)	0.0483	0.0531	0.0620
	(Y . . .Y) Linear	0 0637	0.0701	0.0819
	(Y . . .Y) Non-Linear	0.0734	0 0734	0.1042
$[Pt(NH_3)_4]^{2+}$	(X–Y)	0.0454	0 0468	0.0572
	(Y . . .Y) Linear	0.0610	0 0580	0.0760
	(Y . . .Y) Non-Linear	0.0677	0.0796	0.0960

Table 6. Bastiansen—Morino Shrinkage effect (in Å) for some octahedral Hexaammin Complexes

Complex	Distance	Shrinkage effects		
		T = 0°K	298.15°K	500°K
$[Cr(NH_3)_6]^{3+}$	Y . . . Y long	0.0030	0.0057	0.0088
	Y . . . Y short	0.0008	0.0014	0.0022
$[Co(NH_3)_6]^{3+}$	Y . . . Y long	0.0027	0.0045	0.0070
	Y . . . Y short	0.0006	0.0009	0.0016
$[Ru(NH_3)_6]^{3+}$	Y . . . Y long	0.002F	0.0059	0.0091
	Y . . . Y short	0.0005	0.0010	0.0018
$[Rh(NH_3)_6]^{3+}$	Y . . . Y long	0.0027	0.005F	0.0090
	Y . . . Y short	0.0005	0.0007	0.0015
$[Ir(NH_3)_6]^{3+}$	Y . . . Y long	0 0024	0.0050	0.0079
	Y . . . Y short	0.0004	0.0007	0 0013

The mean-amplitudes of vibration listed in table 5 for octahedral hexaammine, tetrahedral tetraammine and square-planar tetraammine complexes for bonded as well as non bonded distance at temperatures T = 0, 298.15 and 500°K show the expected trend. Bastiansen Morino shrinkage effect for some octahedral hexaammine complexes are listed in table 6

ACKNOWLEDGMENT

Financial assistance provided by CSIR, New Delhi to DKS is thankfully acknowledged.

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